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ADSORPTION AND ACCOMMODATION OF Xe ON Pt{111}

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ABSTRACT

We have recorded real-space images of Xe adatoms on the Pt{111} surface using a scanning tunneling microscope. In the dilute coverage limit, we find nearly all the Xe atoms at step edges. From this observation we deduce a lower limit of hundreds of Ångstroms that Xe atoms scatter across the surface upon adsorption. This result is in sharp contrast to previous studies of metal atom adsorption on metal surfaces in which it is believed that a large fraction of the impinging atoms remain at their point of impact at low surface temperature. For Xe, once the step sites are nearly saturated, point defects on the Pt{111} surface nucleate the growth of compact, incommensurate, rotationally ordered Xe islands. Thus, we have imaged the initiation of the growth of a surface overlayer, and have identified the sites at which this growth begins.

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The phase diagram for the Xe/Pt{111} system has been mapped using He diffraction,¹⁻³ and shows commensurate, incommensurate, and rotated phases as a function of temperature and Xe coverage. Layer by layer growth has been observed up to a coverage of 25 monolayers.³ This system has been the subject of theoretical study involving molecular dynamics simulations and attempts to construct empirical potential surfaces for the adsorbate-surface interaction based upon scattering and thermal desorption data⁴⁻⁸ and also involving structural questions.⁹⁻¹¹

In this letter we report on the adsorption and ordering of Xe on Pt{111} at 4K in the low coverage limit. The low coverage features are apparently inaccessible to (structural) study by He diffraction because of a lack of coherent scattering from a $\sim 12\text{\AA}$ region surrounding substrate steps and adsorbate island edges.^{1,12} We have previously reported on how it is that Xe can be observed using the scanning tunneling microscope (STM).¹³ Here we use this real-space imaging capability to observe several aspects of the adsorption of Xe on the Pt{111} at 4K — accommodation, ordering at step edges, and the nucleation and growth of adsorbate islands. There has been much thought as to the site of adsorption and the sampling of the surface in the adsorption and accommodation processes in the low coverage limit due to the importance of these phenomena in surface chemistry and in epitaxial growth. Until recently, experimentalists have had difficulty studying surface phenomena at low coverage.¹⁴ By working at low temperature, we reduce thermal diffusion to rates which are insignificant on the time scale of our measurements, and are thus able to examine the results of adsorption and accommodation directly *via* real-space imaging with an STM.

In particular, we find that Xe atoms travel hundreds of Angstroms across the surface before reaching their final adsorption site. For metal atom adsorption on metal surfaces at low temperature, it is believed that little or no motion of adsorbing atoms is observed.¹⁶ In the case of Xe, this motion allows the adsorbing atoms to find low energy adsorption sites such as at steps and surface defects, and to form compact islands as described below.



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The experiments were carried out in an ultrahigh vacuum chamber equipped with room temperature crystal preparation and analysis chambers and an STM kept at 4K. The base pressures in the preparation and analysis chambers are in the 10^{-11} torr range, and the pressure in the microscope chamber, which is kept at 4K, is significantly lower due to the negligible vapor pressure of all gases except He and H₂ at 4K. The apparatus will be described in detail elsewhere.¹⁷

The tunneling tip used was a 0.50 mm 80%Pt–20%Rh wire, the end of which was electroetched in molten NaCl. Due to our methods of tip preparation, however, we have no knowledge of the chemical composition nor of the structure of the end of the tip used for tunneling. The Pt crystal was prepared by heating to 850°C in an atmosphere of 10^{-5} torr O₂ followed by many cycles of sputtering with 1 keV Ar⁺ and annealing to 1100°C. The crystal gave sharp LEED patterns and Auger spectra which indicated 0.2–2% carbon impurity in the near surface region. As prepared, the crystal typically had terraces 80–600 Å wide as measured by the STM. Adjacent terraces were separated by monatomic height steps. In any particular area, the steps were spaced fairly regularly and appeared to be along the same crystalline direction. Point defects were present at a density of ~0.02 monolayers (ML), and are discussed further below.

The crystal was dosed by bleeding Xe gas through a sapphire leak valve into the room temperature UHV chamber above the microscope chamber. In order to reach the sample, the Xe atoms have to pass through a 50 cm long by 3.6 cm inner diameter tube which is held at room temperature at one end and 4K at the other. This results in a highly collimated Xe beam impinging upon the sample at 30° from grazing incidence with Xe thermal energies which we estimate to be in the range 100–300K. The Xe flux at the sample was first measured with a quartz crystal microbalance mounted on a shutter above the STM, also kept at 4K. Once the Xe flux was calibrated, the shutter was opened for a time necessary to yield the desired dose to the 4K crystal surface. The coverage was measured by surveying the surface with the STM. This measured coverage was in all cases in good agreement with the calculated dose assuming unity sticking coefficient. This high value of the sticking coefficient is consistent with the trends recorded as a

function of incident energy and angle of a Xe molecular beam impinging on a Pt{111} surface held at 95K by Arumainayagam *et al.*⁶

In Fig. 1 we present an STM image recorded after dosing our Pt{111} crystal to ~ 0.01 ML of Xe. Note that most of the atoms appear along the step edge. We have determined from Laue X-ray diffraction measurements and our occasional ability to image the Pt lattice corrugation that the outward normal to the riser of this step edge is along the $\langle 11\bar{2} \rangle$ direction (so that the step is a close-packed {111} microfacet). By measuring the separation of the peaks in Fig. 1, we find that the Xe atom separation is $5.7 \pm 0.2 \text{ \AA}$. Within the error of the measurement, this is twice the Pt atomic spacing along this step edge ($2 \times 2.78 \text{ \AA} = 5.56 \text{ \AA}$). From this we deduce that in the dilute limit these one-dimensional Xe islands along the $\langle 11\bar{2} \rangle$ steps on the Pt{111} surface are commensurately ordered. The Xe-Xe spacing along the Pt step edge is substantially larger than the 4.4 \AA Xe-Xe spacing in the bulk Xe solid¹⁸ (in the gas phase Xe₂ also has an equilibrium separation of 4.4 \AA).¹⁹ From this we can conclude that at the $\langle 11\bar{2} \rangle$ step, the corrugation of the Xe-Pt interaction potential is sufficiently strong to overcome the Xe-Xe interaction, pulling the Xe atoms apart to form the "2x" structure. Because we have been unable to image the substrate atoms at the step edge, we are unable to determine the adsorption site of the Xe atoms. However, because the peak of the features attributed to Xe atoms line up over 3 \AA from where the downward slope of the step begins to appear in the image, we infer that the row of Xe atoms sit on the lower terrace. An unambiguous determination would require a fuller understanding of the gradual slope observed in images of steps — 80% of the height change occurs over three atomic diameters perpendicular to step edges. The peak heights in the image are not good measures of atomic positions normal to the surface since these are expected to vary with binding site, as has been observed for other adsorbates.²⁰

After dosing with more Xe to bring the coverage up to ~ 0.03 ML, we recorded images such as the one shown in Fig. 2. This shows an island of Xe atoms on a terrace. By counting the peaks in the topographic view shown in Fig. 2b, we infer that there are 13 atoms in the island, making it the

largest we found at this coverage. We note that with the particular surface preparation done for the data presented here, we had a surface concentration of point defects of ~ 0.02 ML. The most prevalent of the point defects on our surface appeared as $\leq 0.1 \text{ \AA}$ depressions in our STM images. We find the surface concentration of these to be dependent upon surface preparation. Subsequent to recording the image shown in Fig. 2, the STM tip was used to move the Xe island away from its initial position. This was done by: positioning the STM tip over the outer perimeter of the island, turning off the feedback loop, moving the tip in towards the surface by 2.6 \AA , changing the bias voltage of the tip to $V = +0.010 \text{ V}$ with respect to the sample for 10 msec, returning the bias voltage to its original value (-0.002 to -0.010 V), and returning the tip to its original height above the surface. This procedure resulted in centering the island about the STM tip with approximately 50% efficiency. Note that a more efficient procedure was subsequently found for moving single Xe atoms about on the Pt{111} and Ni{110} surfaces.²¹ By repeating this procedure, an island could be moved completely away from its initial adsorption site. In all cases when this was done for the Xe islands on the Pt{111} surface, it was found that a depression of $\leq 0.1 \text{ \AA}$ in the STM images lay underneath the initial island positions.

All of the islands we observed were rotated approximately 30° from the close-packed lattice direction. For the island shown in Fig. 2, the *apparent* interatomic spacings within the island vary according to the position within the island of the atoms measured. The measured apparent distance between an "edge" atom and either a "central" atom or another edge atom was $3.7 \pm 0.2 \text{ \AA}$. The Xe-Xe spacings between central atoms was $4.1 \pm 0.2 \text{ \AA}$. There are two possibilities for this difference. First, this could be an indication of a relaxation along the island edge, in which the edge atoms are contracted substantially inward. Second, since the STM measures the contours of constant local density of states (LDOS), the LDOS may be farthest from the surface at positions other than the locations of the edge Xe atoms. Since the central Xe atoms are in a fairly symmetric environment in the crystal surface plane, we do not expect these positions to be displaced from their maxima in the images. However, the edge atoms are in a rather asymmetric environment, and it

would be expected that the electron distribution in this region would respond by redistributing toward the center of the island. This would lead to the apparent peaks shifted toward the center of the island and thus the reduced apparent spacings. Such a reduced peak separation has been observed at certain voltages for the dimers of the reconstructed Si(001) surface by Hamers *et al.*²²

While we have not annealed the overlayer in order to ensure an equilibrium configuration of the Xe, most of the the impinging atoms apparently have enough mobility to find steps in the limit of low coverage and to nucleate into islands at somewhat higher coverages. It should be noted that occasionally in scanning an area of the surface for the first time, we find an individual atom in the middle of a terrace. In this case, the first few line scans over this atom do not move the atom. From this observation we can put a loose upper limit on the diffusion rate across the terraces of at least <0.1 Hz. Such adatoms are relatively uncommon; the great majority of Xe atoms observed at dilute coverage are found condensed along step edges. From this we infer that most impinging Xe atoms either: 1) scatter parallel to the surface from point of impact at least until reaching a step edge, 2) diffuse from point of impact to a step edge, or 3) a combination of the two. For the case of the wider terraces measured, the parallel scatter implies motion on the surface of up to at least 600\AA , the distance between step edges. This is in accord with the calculations of Tully and coworkers, who predict such large parallel motion in the adsorption process.^{5,23} We note that the kinetic energy of the atom immediately after impact may be substantially higher than the incident kinetic energy due to the conversion of a fraction of the adsorption (potential) energy into kinetic energy associated with motion parallel to the surface. Since atoms on terraces such as the one shown in Fig. 3a do not diffuse during a measurement (10 seconds), it is not likely that $>99\%$ of the adsorbed atoms would be able to diffuse at least one half a terrace width, which for the largest terraces observed, implies net motion of at least 300\AA . Therefore, we rule out diffusion as a dominant mechanism for the filling of the step edge adsorption sites. Hopping rates of *ca.* 1 hour^{-1} are predicted for Xe on perfect terraces of Pt{111} at 4K in the calculations of Barker *et al.*⁷ Such a low rate would also be inconsistent with diffusion accounting for the observed distributions of Xe adsorption sites. In the

case where step sites are nearly saturated, either two-dimensional scattering of the type discussed by Sibener and Comsa²⁴ or continuous motion over decorated step edges as proposed by George and coworkers²⁵ must play a role in getting the Xe atoms to their final adsorption sites. As with the He diffraction studies,² we find no evidence of the formation of a second layer at low coverage.

The large range of motion observed for Xe atoms on the Pt{111} surface is in sharp contrast to what is observed for metal atoms adsorbed on metal surfaces. For Ir and other metal atoms impinging at 45° from normal upon an Ir{111} surface at relatively high kinetic energy, little or no lateral motion is observed until the surface temperature is raised so as to give diffusion of the adsorbate atoms.^{15,16} Below the threshold surface temperature for substantial diffusion, most of the impinging atoms are believed to remain at their point of impact.^{15,16} Thus the strongly bound metal atom adsorbates dissipate the energy associated with motion parallel to the surface extremely rapidly.

Using a scanning tunneling microscope we have found that Xe atoms preferred binding sites are along step edges on the Pt{111} surface. We find that impinging atoms scatter hundreds of angstroms across the surface to reach these step sites before the energy corresponding to their motion parallel to the surface plane is accommodated. Further evidence for this long range motion comes from compact Xe islands which grow at point defects on the surface once the step sites are saturated with Xe atoms. This behavior is exactly opposite to what is believed to happen in the adsorption of strongly bound metal atoms on metal surfaces.^{15,16}

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FIGURE CAPTIONS

1. STM image of $100\text{\AA} \times 100\text{\AA}$ region of Pt{111} showing one monatomic height step decorated with Xe atoms. The image was recorded with the tip at $V_{\text{bias}} = -0.005\text{ V}$ and with $I_{\text{tunnel}} = 10\text{ pA}$. The vertical scale is expanded so as to fill the image. The minimum to maximum height difference in the image is 4.15\AA .
2. STM image of $40\text{\AA} \times 40\text{\AA}$ region of Pt{111} showing an island of Xe atoms. The image was recorded with the tip at $V_{\text{bias}} = -0.010\text{ V}$ and with $I_{\text{tunnel}} = 10\text{ pA}$. The minimum to maximum height difference in the image is 2.40\AA .
3. STM images of a $100\text{\AA} \times 100\text{\AA}$ region of the Pt{111} surface with a coverage of $\sim 0.03\text{ ML}$ of Xe recorded with the tip at $V_{\text{bias}} = -0.010\text{ V}$ and a tunnel current of $I = 100\text{ pA}$.
 - a. Initial island configuration.
 - b. After having moved the island to expose an underlying defect. Crosses show the initial positions of features due to Xe atoms.





